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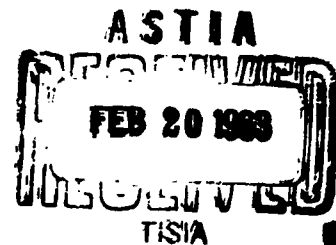
UNIFORM WORK FUNCTION CATHODE STUDIES  
FOR THERMIONIC CONVERTERS

SECOND QUARTERLY REPORT

JANUARY 1963

AERONAUTICAL SYSTEMS DIVISION  
AIR FORCE SYSTEMS COMMAND  
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

BPS 2 - 6799 - 760E - 415604



(PREPARED UNDER CONTRACT NO. AF33(657)-8726 BY ATOMICS INTERNATIONAL,  
A DIVISION OF NORTH AMERICAN AVIATION, INC., CANOGA PARK, CALIFORNIA;  
M. N. HUBERMAN, AUTHOR.)

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## FOREWORD

The work reported here was performed by Atomics International, a Division of North American Aviation, Inc. , under the sponsorship of the Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

This report describes the progress made during the second quarter (12 October 1962 to 12 January 1963) of a program to study the improvement of uniform work functions of thermionic converter emitters under Contract No. AF33(657)-8726. The study program is under the technical supervision of C. C. Weeks of the Thermionics and Thermoelectrics Department of Atomics International.

## ACKNOWLEDGMENTS

The development of techniques of chemical vapor deposition used in this program was performed at San Fernando Laboratories under the direction of Mr. R. Holzl. Mr. R. L. Mohr assisted in the experimental arrangements for converter testing.

The electron micrograph was made by W. G. Brammer and C. E. Rhodes. The x-ray analysis was performed by W. L. Korst. Thanks are due to W. G. Brammer, S. Austerman, and R. Holzl for several informative discussions. The guidance and interest of L. E. Porter of the United States Air Force Aeronautical Systems Division are gratefully acknowledged.

## ABSTRACT

Chemical vapor deposition techniques are being studied as a possible means of producing nonplanar thermionic cathodes having a high degree of uniformity of work function. Vapor deposited molybdenum coatings have been produced by chemical reduction of molybdenum hexafluoride ( $\text{MoF}_6$ ), pyrolysis of molybdenum hexacarbonyl [ $\text{Mo}(\text{CO})_6$ ], and pyrolysis of molybdenum pentachloride ( $\text{MoCl}_5$ ). Plating conditions were varied for each process to determine the effect of plating conditions on the preferred orientations of crystallographic planes parallel to the plating surfaces. Both (100) and (111) preferred orientations have been found for the hexafluoride reductions. The pentachloride samples have strong (100) orientations. The hexacarbonyl samples apparently are not pure molybdenum and do not have the expected molybdenum diffraction pattern.

Oriented depositions will be used in the future to fabricate cylindrical thermionic converter cathodes. Thermionic converters with arc-cast polycrystalline cathodes are being tested to provide data for comparison with converters having vapor deposited cathodes.



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## I. INTRODUCTION

The general purpose of this study program is to improve the efficiency of thermionic converters which have nonplanar geometries. Specifically, the investigation concerns nonplanar emitters of materials having work functions and surface characteristics with a higher degree of uniformity than standard emitter materials used in thermionic converters. This report describes progress of the study from October 12, 1962 to January 12, 1963.

One of the goals of the program reported herein is the chemical vapor deposition of molybdenum coatings of preferred crystallographic orientation on nonplanar surfaces. Consideration of the mechanisms of crystal growth during deposition indicate that variations of vapor deposition parameters should result in modifications of the structure and crystallographic orientation of the deposited layers. Since present theory is inadequate to predict in advance which orientations will be produced, the approach in this program has been to look at the orientations resulting from several different deposition techniques.

Three basic deposition methods were used; chemical reduction of molybdenum hexafluoride ( $\text{MoF}_6$ ), pyrolysis of molybdenum hexacarbonyl [ $\text{Mo}(\text{CO})_6$ ], and pyrolysis of molybdenum pentachloride ( $\text{MoCl}_5$ ). These three methods, in addition to involving different chemical reactions, cover a range of more than  $1300^\circ\text{C}$  in deposition temperatures.

The effects of varying the deposition temperatures were examined. In the case of the hexafluoride reduction, the effect of varying the deposition rate by changing the partial pressure of the hydrogen constituent of the reactant gases was investigated. Increases in the degree of preferred orientation due to increasing the thickness of the deposition layer from 10 to 30 mils were also looked for. In the case of the carbonyl pyrolysis only one 10-mil deposition and one 1/2-mil deposition were performed. The deposits were of such unsatisfactory nature, however, that it was decided to discontinue this method. Since the ultimate goal is fabrication of cylindrical cathodes, cylindrical mandrels of similar dimensions were used for the depositions. The finished products were then cut into approximately 1/2-inch sections for X-ray and metallographic analysis.

## II. GENERAL DISCUSSION OF CRYSTAL GROWTH PROCESSES

Metallic layers produced by chemical vapor deposition are known to have a high percentage of grain growth perpendicular to the deposition surface. For most applications this is an undesirable property causing structural weaknesses. For cathode materials, however, the preferred crystallographic orientations arising from this radial grain growth offer the heretofore unexplored possibility of producing nonplanar emitting surfaces having a more uniform work function than normally exists on randomly oriented polycrystalline emitter surfaces.

In processes such as vapor deposition, crystal growth occurs as the result of condensation of atoms at growth sites on the crystal surface. These growth sites can be at a step at the edge of a partial monolayer, as shown on Figure 1, or at an emergent dislocation such as a screw dislocation, shown on Figure 2. Metal atoms are initially deposited at random surface positions,

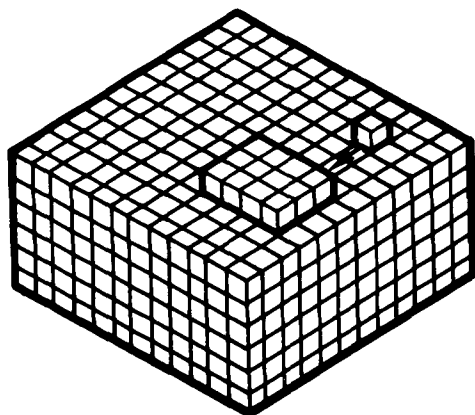


Figure 1. Crystal Growth at Partial Monolayer

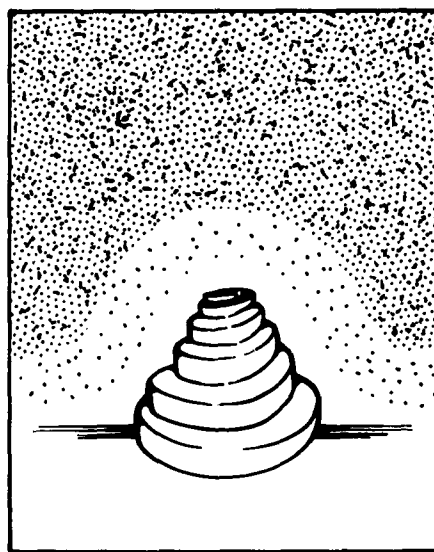


Figure 2. Crystal Growth Due to Screw Dislocation

then migrate at random considerable distances over the surface until they either evaporate or become lodged at a growth site.<sup>1</sup> When the latter occurs, an atom's ability to wander further or evaporate is inhibited by the increased number of bonds it makes in its new position. The process is repeated as

subsequent atoms are added. The net result is the steady advance of the growth step over the surface of the crystal.

In the case of growth steps originating at the edge of partial monolayers, once a layer has been completed a new step can arise as a statistical fluctuation of the newly arriving atoms. In other words, enough migrating atoms can come together to form an island monolayer. If the island exceeds a minimum critical size it will be stable and continue to grow as more atoms arrive.

For a screw dislocation the process is simpler in that the step describes a circular motion, and no further nucleation is needed. Instead there is a spiral growth as the step rotates.

Other dislocation theories exist. A recent review of the state of the theory of whisker growth has been given by Underwood and Powell.<sup>2</sup> The more complicated and less understood process of the growth of crystalline layers has been reviewed by Sherwood and Himes in the same publication.<sup>3</sup> The latter article indicates that while the processes of crystal growth during vapor deposition are understood in a general way, at present it is not known how to modify these processes to any great extent. In the future, however, it should be possible to improve the technology to a point where it would be possible to grow deposits of selected orientation.

Some of the factors that can influence crystal growth processes are:<sup>4</sup>

1. The temperature of the deposition element
2. The partial pressure of the reactant gases
3. The partial pressure of the exhaust gases
4. The orientation of the crystal with respect to the direction of growth.

Items 1 and 2 are inter-related in that each affects the rate of deposition of new atoms on the substrate since (a) temperature affects the reaction rate of the gases that are present and (b) the amounts of gases present are proportional to their partial pressures. The deposition temperature will also affect such factors as the vapor pressure of the deposited material and the surface mobility of deposited atoms which in turn is a major factor in the surface nucleation rate. The partial pressure of the exhaust gas is important in that it controls the reverse reaction rate which can diminish the net deposition growth rate. Finally, the growth rate can vary with crystallographic direction. This

is probably the major factor responsible for producing preferred orientations in thick deposits on non-oriented substrata. The deposition will initially consist of a layer of small randomly oriented nuclei. Nuclei of one orientation will grow more rapidly than others. As the deposition increases in thickness, the more slowly growing nuclei will be enveloped by their more rapidly expanding neighbors. The net result will be a preferred orientation.

### III. DEPOSITION TECHNIQUES

It follows from the foregoing considerations that variations of the deposited parameters can lead to modifications of the crystal growth process which in turn may affect the crystallographic orientations of the deposited layers. The work to be described consists of a program designed to determine the orientations produced by the variations of deposition methods described in Section I.

As previously stated, all depositions are on cylindrical mandrels. For a given deposition an induction furnace is used to heat the mandrel to the desired plating temperature. The induction coil is mounted inside the chamber with its central axis in a vertical position. The mandrel is supported within the coil by means of a wire through the upper end of the mandrel.

The plating temperatures are read by an optical pyrometer which scans the plating surface. The accuracy limits on the plating temperatures are  $\pm 25^{\circ}\text{C}$ . The gas flow rates are measured by either rotameters or orifice meters as shown in the flow diagrams, Figures 3, 4, and 5. The flow meter readings are accurate to  $\pm 5\%$ .

Prior to each deposition the chamber is roughed down by a mechanical pump. A water pump is used during the depositions, however, because of the corrosive nature of the gases involved in the plating operation.

#### SURFACE PREPARATION

No cutting oil is used in machining and grinding the molybdenum mandrels. Each mandrel is cleaned in sodium hydroxide solution prior to insertion into the deposition chamber. After the mandrel is in position, the chamber is evacuated to 1 torr absolute and the mandrel heated to  $100^{\circ}\text{C}$  higher than the deposition temperature or  $850^{\circ}\text{C}$ , whichever is greater. The entire system is then flushed with hydrogen for 15 minutes with the mandrel still at its elevated temperature.

The mandrel is then adjusted to the plating temperature with hydrogen still flowing through the system. After the correct plating temperature is obtained, the hydrogen flow rate is either adjusted to its proper value for the reduction of molybdenum hexafluoride or shut off completely for the depositions not requiring hydrogen. Finally, a metered flow of reactant gas is introduced into the system.

## CHEMICAL REDUCTION OF MOLYBDENUM HEXAFLUORIDE

In this method molybdenum hexafluoride is chemically reduced on the heated mandrel by the action of hydrogen and a proprietary additive. The flow diagram for this method is shown in Figure 3. Electrically heated tubing was used to counteract refrigeration of expanding gases leaving their containers.

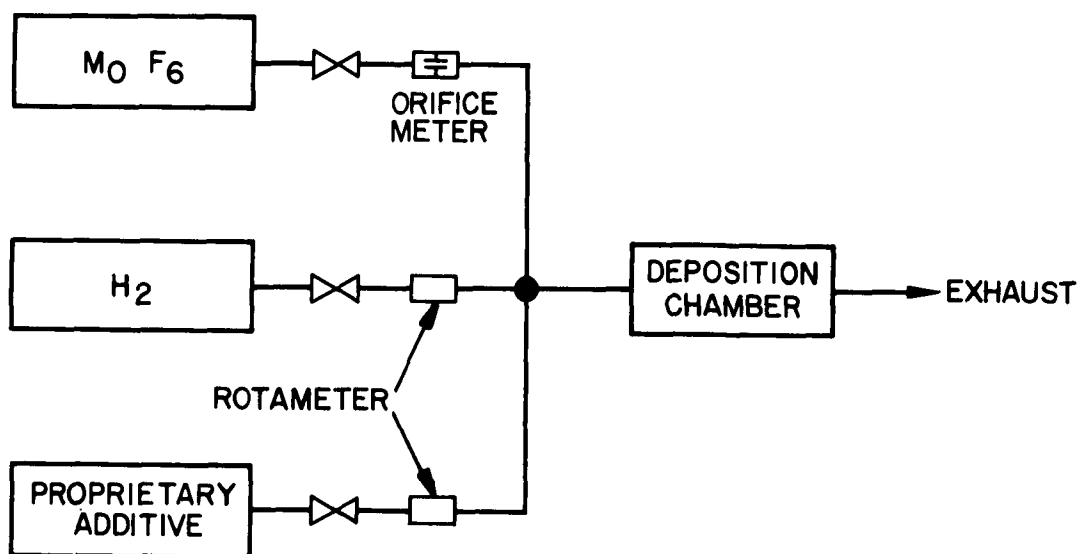


Figure 3. Flow Diagram for Chemical Reduction of Molybdenum Hexafluoride

Fifteen samples were produced by this method. The deposition parameters are listed in Table I. Samples 1 through 3 were deposited on 3/8-inch diameter molybdenum rods which had large surface grain structures due to previous histories of being heated almost to the point of melting for extended periods of time. Samples 2 and 3 were subsequently machined to give a surface of homogenous appearance. A discussion of these samples was previously presented.<sup>5</sup> Sample 25 was deposited on a graphite rod, 3/8-inch in diameter, to determine the effect of a graphitic substrate on deposition orientation.

The remainder of the hexafluoride reduction samples were deposited on ground arc-cast polycrystalline molybdenum rods 4 inches long by 0.305 inch in diameter. These rods are of the same diameter as the mandrels that will subsequently be used for the fabrication of vapor-deposited cathodes.



TABLE I  
CHEMICAL REDUCTION OF MOLYBDENUM HEXAFLUORIDE

Sample No.	Substrate	Temp. °C	MoF <sub>6</sub> H <sub>2</sub> FLOW (liters/min)	Max. Dep. Rate (Mils/Min)	Thickness Mils	Tank Pressure (In. Hg gauge)
1	large grained Mo rod	750	1 3	0.5	11	
2	machined Mo rod	700	1 3	0.4	7-8	
3	machined Mo rod	800	1 3	0.2	3-1/2 4-1/2	
4	machined Mo rod	850	1 3	1.5	10	24
5	machined Mo rod	900/925	1 0.85	1.8	10	26
6	machined Mo rod	700/750	1 3	0.6	10	23
7 <sup>a</sup>	machined Mo rod	850	1 3.4	1.8	30	24
8 <sup>a</sup>	machined Mo rod	750	1 3.4	1.1	30	24
9	machined Mo rod	800/850	1 3.4	1.5	10	24
10	machined Mo rod	800/850	1 3.4	1.5	10	24
11	flat and round <sup>b</sup>	700/750	1 4	0.9	10	23

Notes

a - To determine orientations of thicker depositions.

TABLE I (Continued)

Sample No.	Substrate	Temp °C	MoF <sub>6</sub> M <sub>2</sub> FLOW (liters/min)	Max. Dep. Rate (Mils/Min)	Thickness Mils	Tank Pressure (In. Hg gauge)
13	flat and round <sup>b</sup>	850	1 3.4	1.7	10	24
15 <sup>c</sup>	machined Mo rod	725	1 3.5	1.6	10	26
16 <sup>c</sup>	machined Mo rod	725	1 8	0.6	10	24
25	graphite	800/850	1 3	0.8	8	20

Note

- b - Semicylindrical mandrel to check curved surface x-ray results vs. flat surface results.  
c - To determine effects of varying deposition rate at constant deposition temperatures.

Samples 11 and 13 were machined flat on one side to form semicylinders. Each of these samples thus provided identically deposited flat and round surfaces to be used as a check on the reliability of the curved surface x-ray data.

Samples 1 through 6 and 25 were produced by an axial gas flow upward along the side of the rod as the rod was rotated at 18 rpm. For the remainder of the hexafluoride depositions the gas flow was from 1/8 inch slot along the length of a 1/4 inch I. D. Alundum tube positioned parallel to the rotating sample.

#### PYROLYSIS OF MOLYBDENUM HEXACARBONYL [Mo(CO)<sub>6</sub>]

The flow diagram for pyrolysis of molybdenum hexacarbonyl is shown in Figure 4. A carrier stream of wet argon was produced by bubbling argon through water at 40°C. The wet stream was subsequently transported through heated tubing to prevent condensation of the water vapor. A pot of carbonyl was placed in a 60°C temperature bath at the bottom of the deposition chamber. The argon stream was passed through the pot to transport the subliming carbonyl upward to the mandrel, which in this case was suspended in a horizontal position immediately above the pot. In this case the samples were not rotated during deposition. This was because of the necessity for attaching a thermocouple to one end of the rod in order to measure the low temperatures at which the carbonyl pyrolysis was carried out.

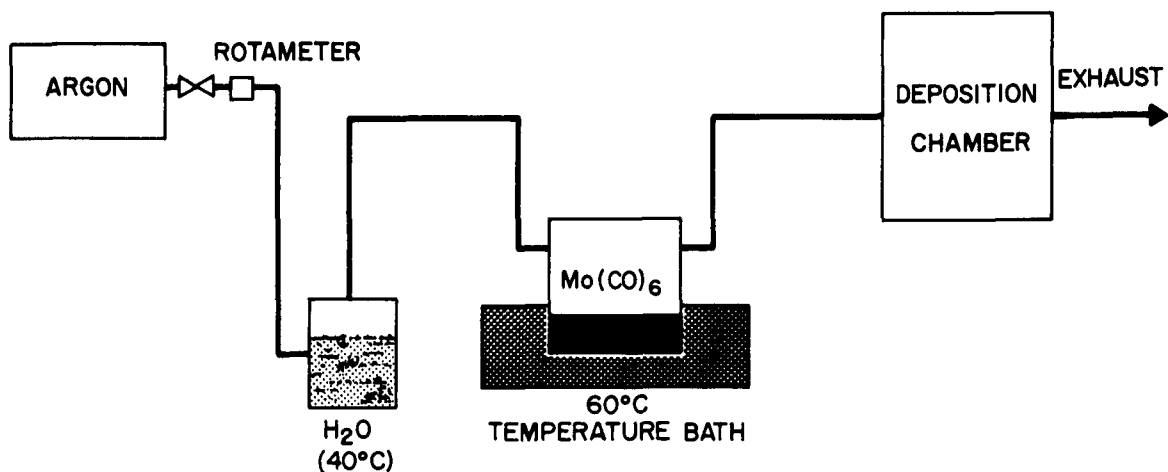


Figure 4. Flow Diagram for Pyrolysis of Molybdenum Hexacarbonyl

Sample 12 was a 10-mil deposition at 250°C. The deposition rate was 2 mils per hour. Sample 14 was a 1/2-mil deposition at 200°C. The deposition rate in this case was 1.5 mils/hour. In both cases the pressure in the deposition chamber was 1 torr. The samples were deposited on ground arc-cast polycrystalline molybdenum rods 4 inches long by 0.305 inch in diameter.

Both deposits were of an unsatisfactory nature, as discussed in Section IV. Consequently, fabrication of samples by this method was discontinued.

#### PYROLYSIS OF MOLYBDENUM PENTACHLORIDE ( $\text{MoCl}_5$ )

In the pyrolysis of molybdenum pentachloride a pot of molybdenum powder heated to 450°C was placed at the bottom of the deposition chamber. A mixture of 0.3 liters per minute of chlorine and 3 liters per minute of argon passed through the powder to form molybdenum pentachloride. The pentachloride was then pyrolytically decomposed on the rotating mandrel shown in Figure 5. The pressure in the deposition chamber was 30 torr. Samples 17, 18, and 19 were 10-mil depositions at temperatures of 1100, 1300, and 1500°C respectively. The corresponding deposition rates were 0.2, 0.8, and 0.6 mils per minute. The samples were deposited on ground arc-cast polycrystalline molybdenum rods 4 inches long by 0.305 inch in diameter.

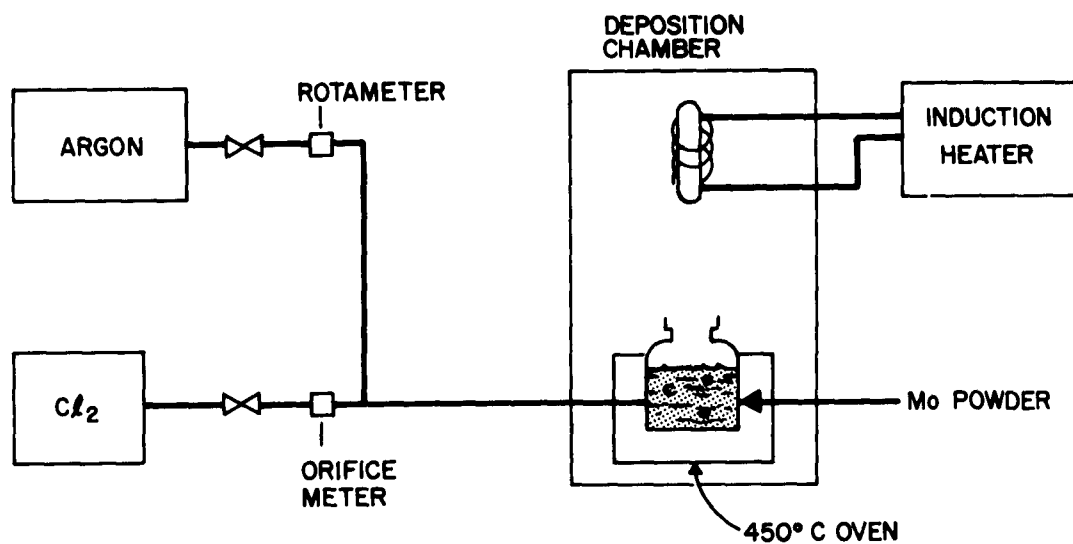


Figure 5. Flow Diagram for Pyrolysis of Molybdenum Pentachloride

#### IV. STRUCTURE OF DEPOSITIONS

Adherent depositions were achieved for all hexafluoride reduction and pentachloride pyrolysis samples. Neither carbonyl pyrolysis sample turned out well. Sample 12 was non adherent. The deposition could be flaked off with a finger nail. The flakes were extremely brittle and easily crumbled. Sample 14, which was nominally a 1/2-mil deposition, only partially coated the mandrel.

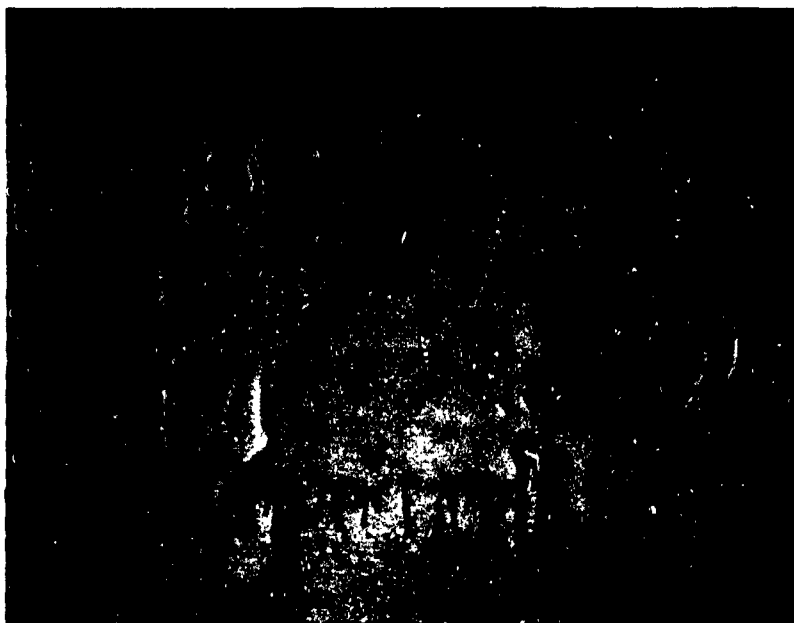
Transverse cross sections of the depositions were polished, etched, and photomicrographed as shown in Figure 6. Columnar grain growth is evident for all pentachloride and hexafluoride samples. Sample 12, the 10-mil carbonyl deposition has a completely different layered structure. Possibly the deposition did not grow continuously but formed intermediate layers of either molybdenum granules or impurities.

Some of the photographs (Sample 8 is a good example) show an initially small grained structure that develops into a smaller number of large diameter columnar grains as the deposition grows. This is in agreement with the previously discussed theory of initially random nucleation producing a preferred orientation because of differences in growth rates.

The role of epitaxy in these depositions is an interesting consideration. The different growth rates in different crystallographic directions should cause an initially epitaxial deposit on a randomly oriented substrate to develop a preferred orientation if the initial grain diameters are small in comparison to the deposition thickness. Sample 10 appears to be an example of this process. There is no well defined boundary between the substrate and the deposit but rather what looks like an epitaxial growth of the substrate grains into the deposition layer. Many of the grains subsequently terminate as they are overgrown by adjacent grains.

There are two possible ways of utilizing vapor depositions in the fabrication of cathodes. One way is to start with an oversized deposition and then electropolish the surface down to the required dimensions. The second possibility is to use "as deposited" surfaces since the deposition process may tend to expose certain preferred surface planes. The surfaces of the depositions produced in this study have coarse granular appearance. Microscopic examination shows the surface texture to be due to protruding pyramidal grains. Figure 7 is a

transmission electron micrograph of a replica of one of these surfaces. Although the pyramid in this figure is six-sided, three- and four-sided pyramids also frequently occur.



Sample 1

Sample 2



Figure 6a. Photomicrographs of Vapor Depositions



Sample 3



Sample 4

Figure 6b. Photomicrographs of Vapor Depositions



Sample 5



Sample 6

Figure 6c. Photomicrographs of Vapor Depositions





Sample 7



Sample 8

Figure 6d. Photomicrographs of Vapor Depositions

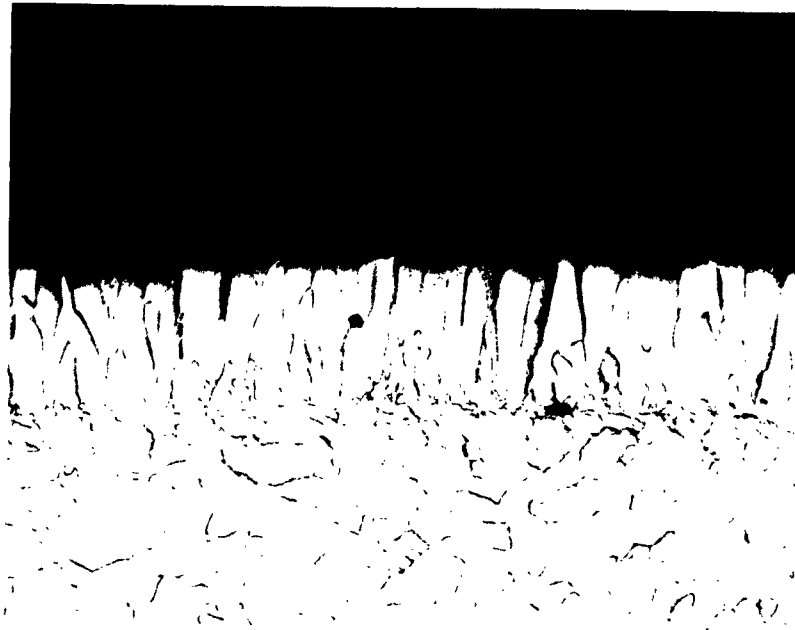


Sample 9



Sample 10

Figure 6e. Photomicrographs of Vapor Depositions



Sample 11

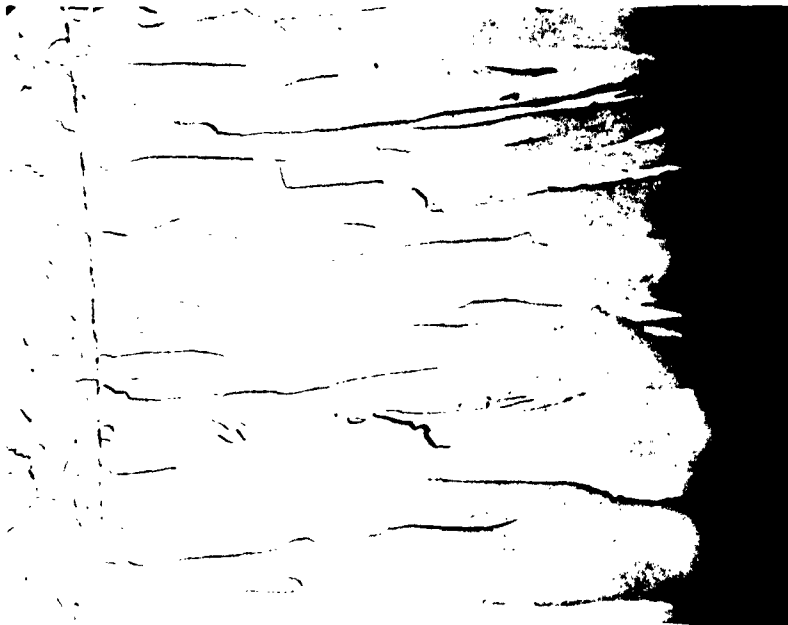


Sample 12

Figure 6f. Photomicrographs of Vapor Depositions

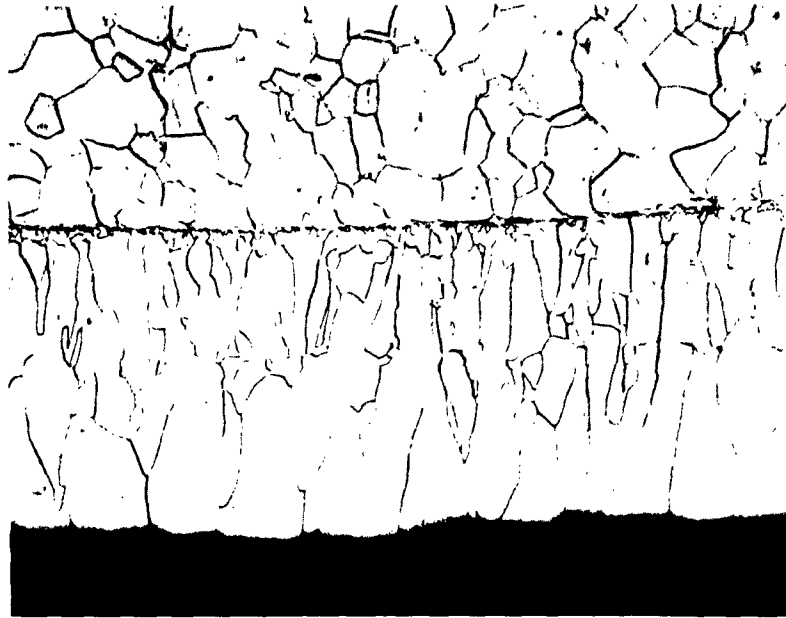


Sample 13



Sample 15

Figure 6g. Photomicrographs of Vapor Depositions

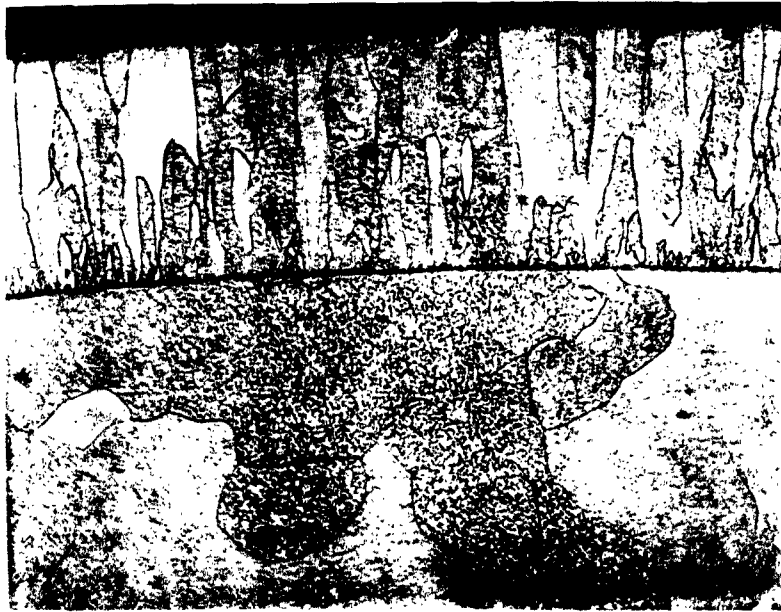


Sample 16

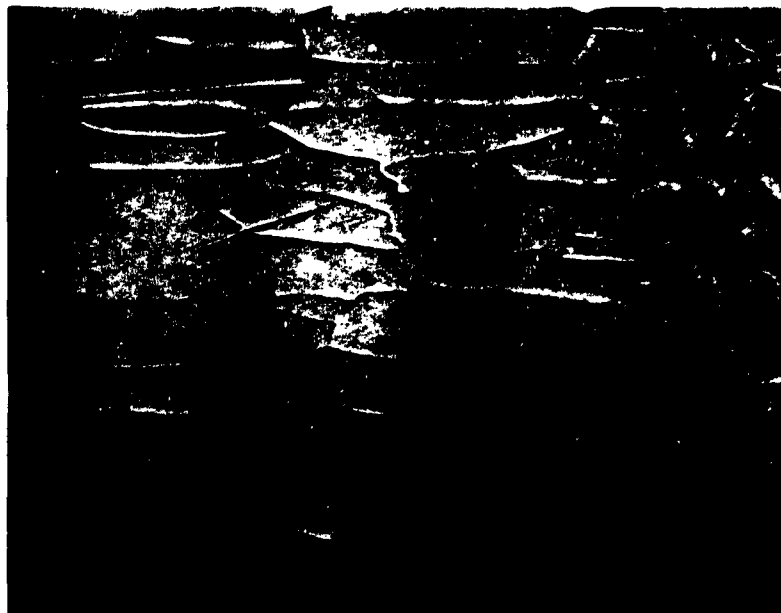


Sample 17

Figure 6h. Photomicrographs of Vapor Depositions

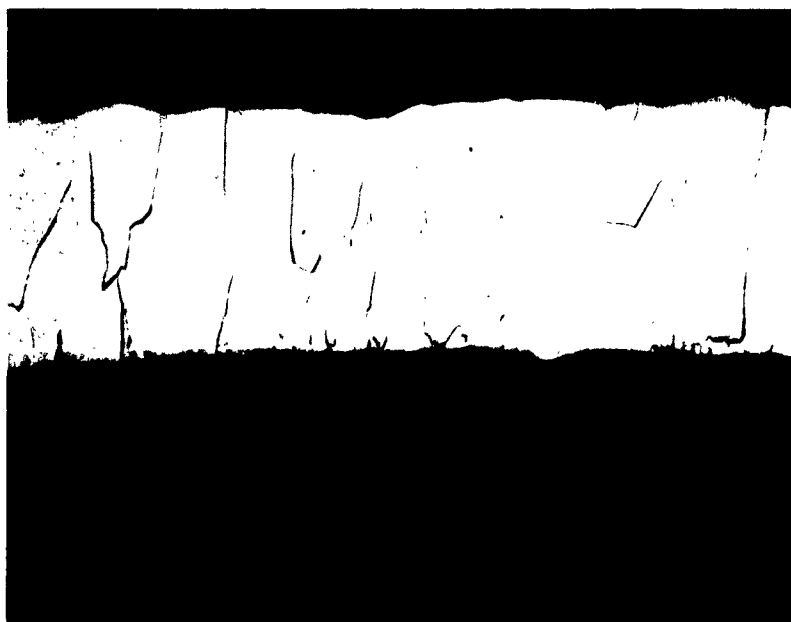


Sample 18



Sample 19

Figure 6i. Photomicrographs of Vapor Depositions



Sample 25

Figure 6j. Photomicrographs of Vapor Depositions

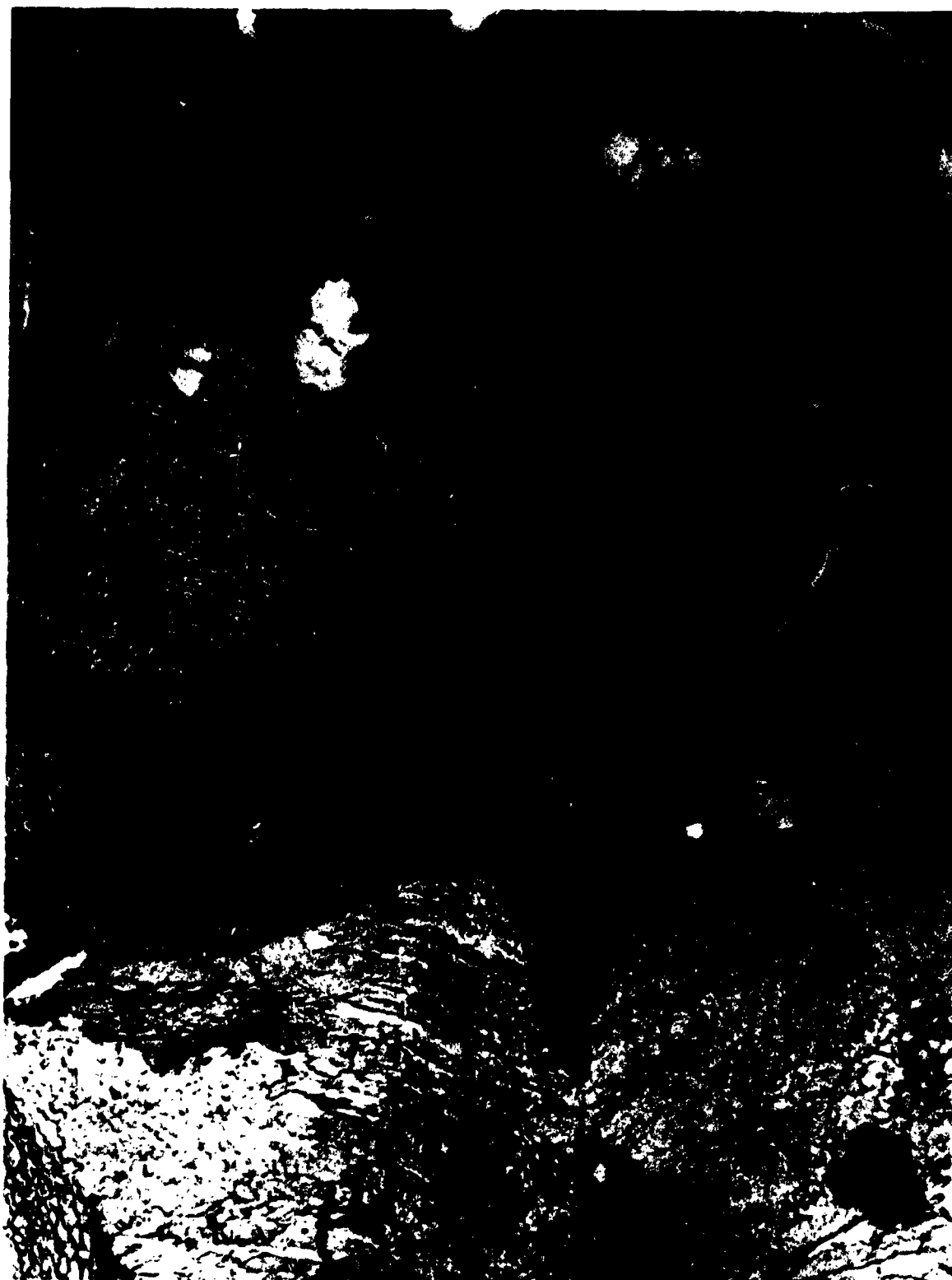


Figure 7. Electron Micrograph of Deposition Surface Replica



## V. X-RAY ANALYSIS

X-ray analysis of the samples to determine preferred orientations of crystallographic planes parallel to the deposition surfaces is near completion.

### METHOD

A rod to be examined is placed in a North American Phyllips type 42202 wide range goniometer with its axis perpendicular to the plane of the incident and reflected beams as shown in Figure 8. The detector and sample are positioned so that the incident and reflected beams are at equal angles to the surface tangent plane. Thus only reflections from planes parallel to the surface are detected. Figure 9 illustrates the basic focusing geometry. The beam is that of a collimated line source parallel to the cylinder axis. Narrow  $1/4^\circ$  collimating slits give the beam a height of approximately 1 mm at the sample. A copper anode and nickel filter combination are used to provide a  $\text{Cu K}\alpha$  beam. The reflected intensity is recorded on a strip chart recorder as a function of incident angle.

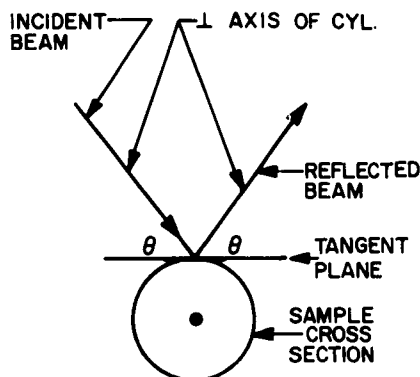


Figure 8. X-ray Sample Geometry

Randomly oriented cylindrical standard samples are prepared by mixing powdered molybdenum and glue to form thin surface layers on a  $3/8$ -inch diameter plastic rod and on a  $1/4$ -inch diameter glass rod. Table II compares the intensities obtained from these samples with the NBS pattern<sup>6</sup> for a randomly oriented sample. The agreement is fairly good and indicates that any departures from these relative intensity patterns for vapor deposited rods will indeed be due to preferred orientations.

TABLE II  
PEAK HEIGHTS FOR RANDOMLY  
ORIENTED SAMPLES

hkl	3/8" rod	1/4" rod	NBS
110	76	80	100
200	14	16	21
211	20	22	39
220	3	4	11
310	7	10	17
222	1	2	7
321	*	*	26

\* At high angles (about 132.5°); not scanned.

Samples 11 and 13 had both flat and round deposited surfaces as previously discussed. Although the orientation was different for the two rods, in each case there was agreement between the orientations found for the flat surface and for the round surface. This served as a further check on the reliability of the curved surface data.

## RESULTS

The results to date of X-ray analysis of the samples are listed in Table III. Each sample was scanned at several positions around the circumference to determine uniformity of preferred orientations and to insure that a good statistical sample of reflecting grains was included.

A measure of the degree of orientation of a given plane (hkl) parallel to the surface can be obtained from the quantity  $I_{hkl} / \Sigma I_{hkl}$ . Here  $I_{hkl}$  is the peak intensity from the (hkl) plane and  $\Sigma I_{hkl}$  is the sum of peak intensities over all planes. Table IV lists the values of  $I_{hkl} / \Sigma I_{hkl}$  obtained from the data of Table III by averaging overall positions of each sample. For comparison, the same quantity has been calculated for the 3/8-inch random sample of Table II.

The Bragg reflections for pure crystalline molybdenum were not observed for the carbonyl samples. Instead a number of peaks of very low intensity were observed at other diffraction angles. The analysis of these peaks is not yet

TABLE III  
X-RAY DIFFRACTION INTENSITIES FOR VAPOR DEPOSITED SAMPLES

Sample No.	hkl	POSITIONS <sup>1</sup>						Sample No.	hkl	POSITIONS <sup>1</sup>					
		1	2	3	4	5	6			1	2	3	4	5	6
1	110	2	7	3				7	110	0	0	3			
	200	13	11	16					200	1	0	0			
	211	63	9	4					211	18	4	2			
	220	0	0	0					220	0	0	0			
	310	2	9	1					310	0	0	0			
	222	10	2	0					222	53	190	130			
3	110	52	5	4	4		81	8	110	3	3	4			
	200	7	2	0	13	1	9		200	0	0	0			
	211	63	4	56	6	22	19		211	19	30	3			
	220	17	0	0	0	0	13		220	0	0	0			
	310	7	0	0	0	0	0		310	0	0	0			
	222	8	47	21	16	35	70		222	38	84	144			
4	110	0	0	0				9	110	2	6	2			
	200	~180	~560	~600					200	20	91	51			
	211	8	0	11					211	13	16	83			
	220	0	0	0					220	0	0	0			
	310	2	28	90					310	3	11	8			
	222	0	0	0					222	90	116	55			
5	110	3	4	0				10	110	0	2	0			
	200	1	0	0					200	0	0	0			
	211	8	8	6					211	9	4	44			
	220	0	0	0					220	0	0	0			
	310	0	0	0					310	0	0	0			
	222	83	59	112					222	15	104	3			
6	110	0	0	0				11	110	0	0	0 <sup>3</sup>			
	200	2	0	0					200	~120	~140	~160			
	211	1	7	17					211	14	3	1			
	220	0	0	0					220	0	0	0			
	310	0	0	0					310	17	25	0			
	222	75	22	10					222	3	1	12			

TABLE III (Continued)

Sample No.	hkl	POSITIONS 1						Sample No.	hkl	POSITIONS 1					
		1	2	3	4	5	6			1	2	3	4	5	6
13	110	0	0	0 <sup>3</sup>	0 <sup>3</sup>			16b <sup>2</sup>	110	0	0	0			
	200	0	0	0	0				200	0	0	0			
	211	4	3	0	0				211	1	0	6			
	220	0	0	0	0				220	0	0	0			
	310	0	0	0	0				310	0	0	0			
	222	95	85	26	20				222	75	100	50			
15a <sup>2</sup>	110	0	0	0	0			17	110	0	0	0			
	200	5	1	0	0				200	165	180	180			
	211	0	1	0	0				211	0	0	0			
	220	0	0	0	0				220	0	0	0			
	310	0	0	0	0				310	0	0	0			
	222	105	150	73					222	0	0	0			
15b <sup>2</sup>	110	2	1	2				18	110	0	0	0			
	200	0	1	1					200	140	120	150			
	211	22	2	2					211	0	0	1			
	220	0	1	0					220	0	0	0			
	310	1	2	0					310	1	0	0			
	222	120	150	200					222	5	20	3			
16a <sup>2</sup>	110	15	6	3				19a <sup>2</sup>	110	0	0	0			
	200	86	53	80					200	80	95	95			
	211	17	35	30					211	0	0	0			
	220	1	0	0					220	0	0	0			
	310	51	12	22					310	0	0	0			
	222	3	2	1					222	0	0	6			

## Notes:

1. For each sample the different positions correspond to rotations of the sample around its axis.
2. Samples 15a and b, 16a and b, 19a and b refer in each case to separate longitudinal sections cut from the same original rod.
3. Position 3 on sample 11 and positions 3 and 4 on sample 13 are on flat side of samples.

TABLE III (Continued)

Sample No.	hkl	POSITIONS 1						hkl	POSITIONS 1					
		1	2	3	4	5	6		1	2	3	4	5	6
19b <sup>2</sup>	110	0	0	0				110	0	0	0			
	200	57	48	15				200	~160	~228	~180			
	211	1	0	0				211	0	5	0			
	220	0	0	0				220	0	0	0			
	310	0	0	0				310	22	18	21			
	222	1	2	60				222	0	0	0			

Notes:

1. For each sample the different positions correspond to rotations of the sample around its axis.
2. Samples 15a and b, 16a and b, 19a and b refer in each case to separate longitudinal sections cut from the same original rod.
3. Position 3 on sample 11 and positions 3 and 4 on sample 13 are on flat side of samples.

completed, but they apparently are due to an impurity deposit having a face-centered cubic structure.

More time is needed to analyze the data but the following general observations may now be made.

1. Preferred orientations have been obtained
2. The hexafluoride reduction samples exhibit (111) orientations in most cases but a few (100) orientations also occur
3. The pentachloride pyrolysis samples all exhibit strong (100) orientations
4. The carbonyl depositions were not pure molybdenum.

TABLE IV  
CALCULATED VALUES OF  $I_{hkl} / \sum I_{hkl}$

PLANE	SAMPLE NUMBER						
	1	3	4	5	6	7	8
110	0.079	0.255	0.000	0.025	0.000	0.007	0.030
200	0.263	0.055	0.906	0.004	0.015	0.002	0.000
211	0.500	0.291	0.013	0.077	0.187	0.060	0.158
220	0.000	0.051	0.000	0.000	0.000	0.000	0.000
310	0.079	0.012	0.081	0.000	0.000	0.000	0.000
222	0.079	0.337	0.000	0.894	0.799	0.930	0.811
	9	10	11	13	15A	15B	16A
110	0.018	0.011	0.000	0.000	0.000	0.010	0.056
200	0.286	0.000	0.847	0.000	0.018	0.004	0.525
211	0.197	0.315	0.036	0.030	0.003	0.051	0.197
220	0.000	0.000	0.000	0.000	0.000	0.002	0.002
310	0.039	0.000	0.085	0.000	0.000	0.006	0.204
222	0.160	0.674	0.032	0.970	0.979	0.927	0.014
	16B	17	18	19A	19B	25	3/8" Random
110	0.000	0.000	0.000	0.000	0.000	0.000	0.628
200	0.000	1.000	0.932	0.978	0.652	0.896	0.116
211	0.030	0.000	0.002	0.000	0.005	0.008	0.165
220	0.000	0.000	0.000	0.000	0.000	0.000	0.025
310	0.000	0.000	0.002	0.000	0.000	0.096	0.058
222	0.970	0.000	0.064	0.022	0.342	0.000	0.008

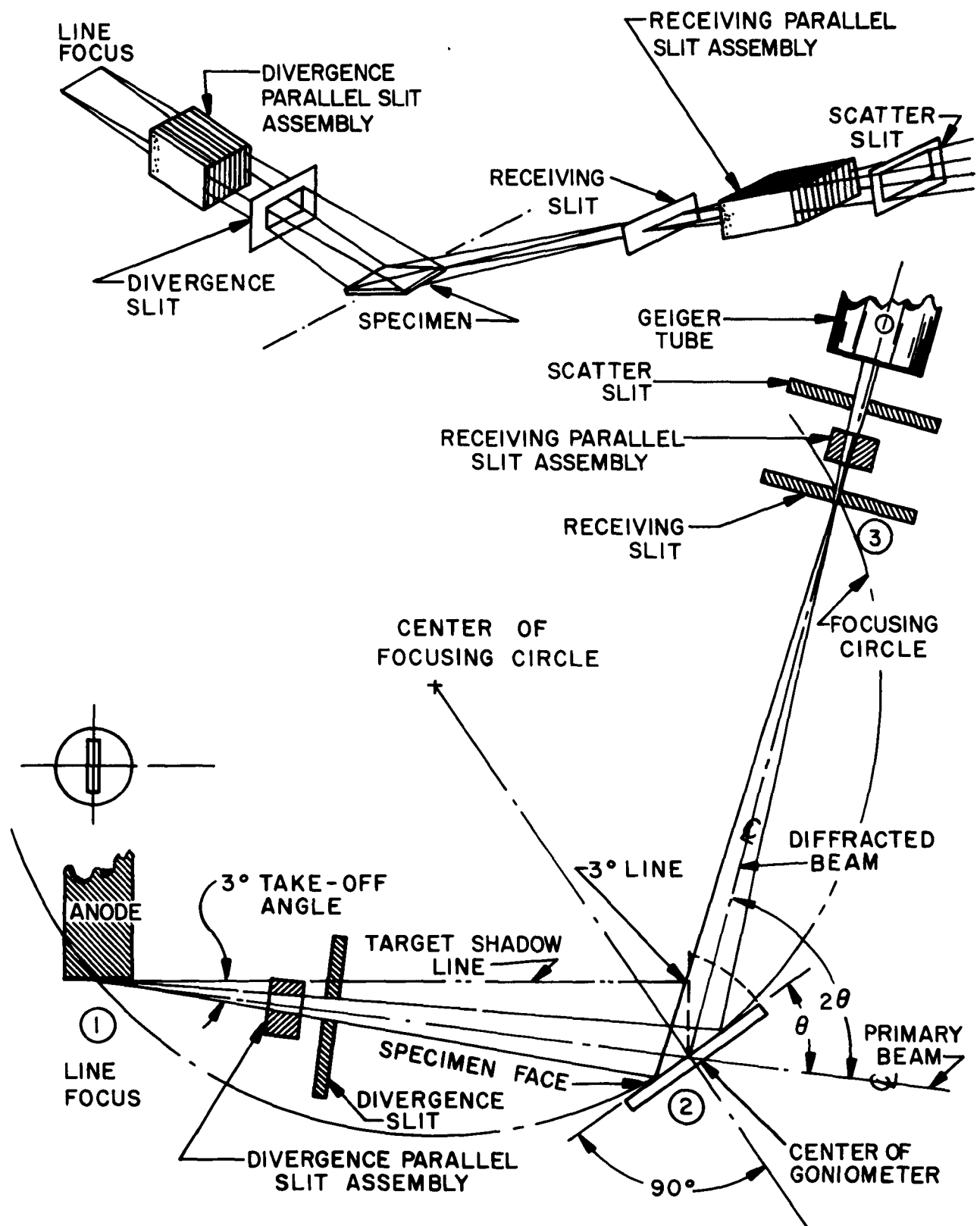


Figure 9. Basic Focusing Geometry

## VI. CONVERTER TESTING

The first converters with standard arc-cast polycrystalline cathodes have been assembled and data is being taken for comparison with subsequent converters having vapor-deposited cathodes.

In order to evaluate fully the results of the converter testing it would be desirable to have a separate means of measuring the uniformity of work function of the vapor-deposited cathodes. Work has begun on an electron lens system for projecting magnified emission patterns from cathode surfaces on a fluorescent screen.



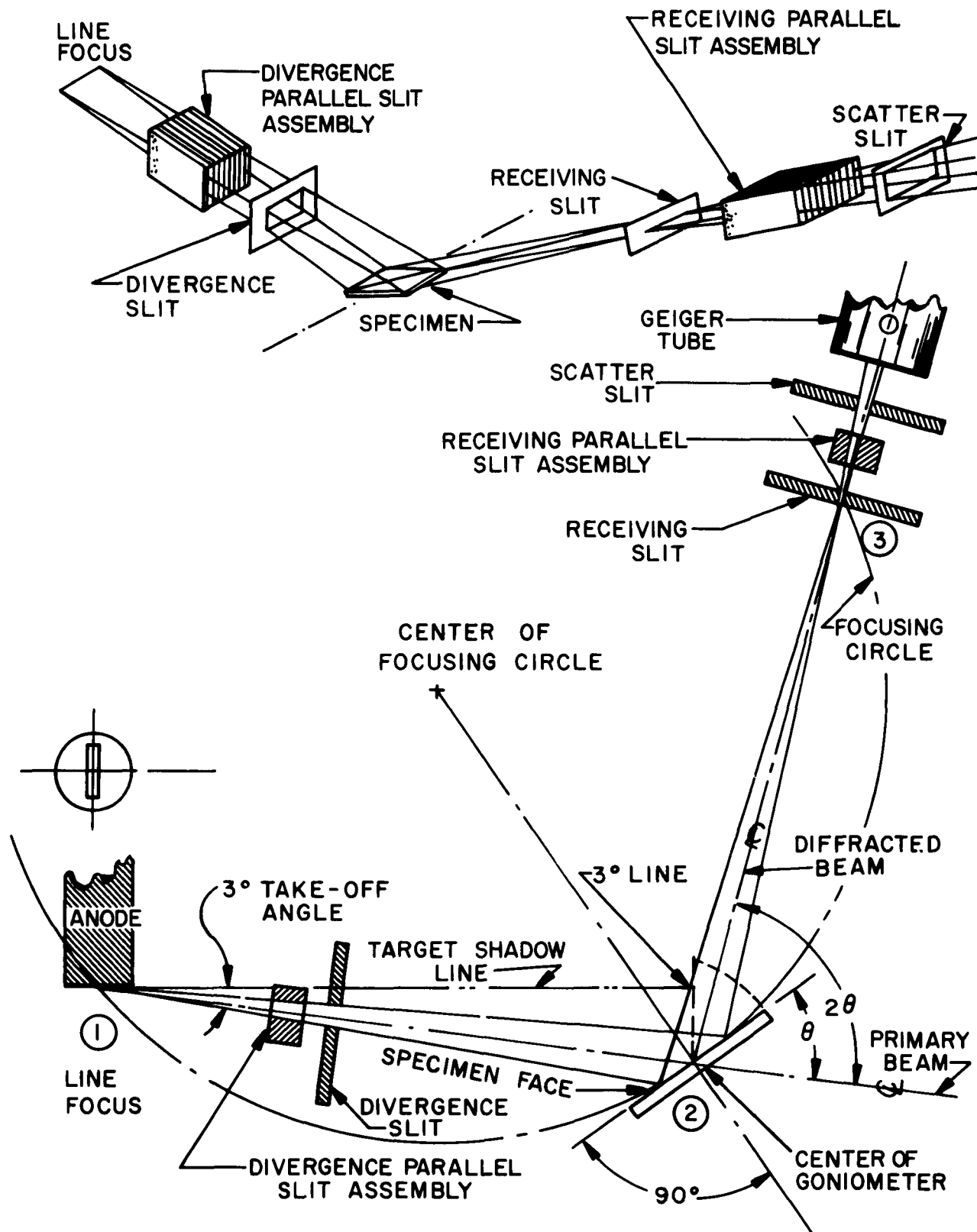


Figure 9. Basic Focusing Geometry

## VI. CONVERTER TESTING

The first converters with standard arc-cast polycrystalline cathodes have been assembled and data is being taken for comparison with subsequent converters having vapor-deposited cathodes.

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## VII. CONCLUSIONS

Chemical vapor deposition is capable of producing preferred orientations in molybdenum cathodes. Chemical reduction of molybdenum hexafluoride produces preferred orientations of (111) planes parallel to the deposition surface in most cases but a few (100) orientations also occur. The pentachloride pyrolysis samples all exhibit strong (100) orientations.

It should be possible to utilize the hexafluoride or pentachloride deposition methods to fabricate cathodes having a high percentage of either (100) or (111) emitting surfaces.

## VIII. RECOMMENDED PROGRAM FOR THE THIRD QUARTER

Analysis of the x-ray data will be completed to determine the vapor deposition techniques most capable of producing preferred orientations. Cathodes will be fabricated by these techniques and incorporated into diodes for testing.

Some time will have to be spent on determining a suitable method of finishing the cathode surfaces since conventional grinding or machining techniques break up the crystalline structure at the surface. A study will be made of electropolishing, which is probably the best way to finish these surfaces without disturbing the underlying crystal structure.

The measurements on polycrystalline cathodes will be completed and testing of vapor deposited cathodes will begin.

Work will continue on a mapping device for determining the uniformity of emission from cathode surfaces.

## REFERENCES

1. W. K. Burton, N. Cabrera and F. C. Frank, Phil. Trans. Roy. Soc. A243, 299 (1950)
2. E. E. Underwood and C. F. Powell, "The Science of Whisker Growth," Chemical Vapor Deposition DMIC Report 170, (June 4, 1962). See also Charles Kittel "Introduction to Solid State Physics" 2nd Edition, John Wiley & Sons (1956) Chapter 19
3. E. M. Sherwood and R. C. Himes, "The Growth of Crystalline Films and Layers by Chemical Vapor Deposition," Chemical Vapor Deposition DMIC Report 170, (June 4, 1962)
4. Robert F. Rolsten, "Iodide Metals and Metal Iodides," John Wiley & Sons, (1961)
5. M. N. Huberman, "Uniform Work Function Cathode Studies for Thermionic Converters, First Quarterly Report," AI-7801, Atomics International Inc., (October, 1962)
6. National Bureau of Standards Circular 539, Vol 1, p 20

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